Orbital dependence of superexchange interaction in charge-ordered manganites

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Abstract. The current investigation is devoted to the theoretical study of orbital structure influence upon magnetic subsystem in half-doped charge-ordered manganites. The main interaction of magnetic subsystem is superexchange interaction. It forms spin-wave dispersion dependencies. Because of charge and orbital ordering, there are a lot of superexchange parameters in these compounds. That makes the dispersion rather complicated. This work clarifies some features of dispersion in terms of orbitally-dependent superexchange interactions.

1. Introduction

The manganite crystals $R_{1-x}A_xMnO_3$ (where R^{3+} is a rare earth ion, A^{2+} is an alkaline earth ion, and x is a doping rate) are known not only as colossal magnetoresistance (CMR) compounds. These crystals have a lot of properties forming peculiar magnetic structures, such as low-dimensional, frustrated or incommensurate orderings [1]. The set of perovskite-like crystals are extended by layered compounds like $R_{1-x}A_{1+x}MnO_4$ and $R_{2-2x}A_{1+2x}Mn_2O_7$. For same doping rates (x=0.5, 0.25, 0.75, 0.667 and so on), the charge-ordering model is applied to describe an insulating state. The wide range of models are created and developed for explanation of complicated spin arrangements [2].

The focus of this paper is on half-doped charge-ordered (CO) manganites with 3D perovskite structure $R_{0.5}A_{0.5}MnO_3$, layered perovskite $R_{0.5}A_{1.5}MnO_4$ and bilayer perovskite $RA_2Mn_2O_7$. The distorted crystalline structures of these compounds are combined with charge, orbital and magnetic structures [3–6]. The CE-type magnetic structure is the result of complicated correlation between these subsystems [1, 7]. The estimation of magnetic interactions dependent upon an orbital ordering was made mainly using Neel temperatures [7, 8]. Recent experimental studies of spin-waves dispersion dependencies allow estimating exchange parameters between different manganese pairs [9–11] more precisely.

In present investigation, the orbital dependence model [7] of superexchange (SE) parameters is improved using experimental data [9–11] and spin-wave dispersion dependencies are calculated. The aims of the study are within the framework of improved model of orbitally dependent superexchange interaction, to compare calculated spin-waves spectra with experiments [9–11] and to find out the influence of the type of exchange pair at the dependence peculiarities.

2. Method

The calculation of spin wave spectra is divided into three steps. First, using the crystalline and charge structures from published experiments, the orbital ordering in trivalent manganese sublattice is calculated. This step could give approximate results in case of strong distortions [12] or lack of detailed experimental data [8]. The second step is determination of magnetic interactions parameters [7, 8, 13, 14]. Thirdly, the magnetic excitation spectra are calculated [15].

2.1. Orbital and charge structures of half-doped manganite

The half-doped charge ordered manganites with common formulae $R_{0.5}A_{0.5}MnO_3$, $R_{0.5}A_{1.5}MnO_4$, $RA_2Mn_2O_7$ have a peculiar charge structure. The additional charge carriers due to non-isovalent rare-earth doping localize on manganese ions. Mn^{3+}/Mn^{4+} ions arrangement is of "chessboard-type" [3–6]. Mn^{3+} ions have degenerated ^5E ground state in symmetric O^{2-} octahedral coordination. Due to Jahn-Teller effect, the oxygen octahedra are distorted, and the degeneration of the ground state is removed. The orbital state of Mn^{3+} ion is dependent of its place in the crystalline lattice [13]:

$$\Psi_i = \left|\cos\frac{\Theta_i}{2}\right|\left|\theta\right\rangle_i \pm \left|\sin\frac{\Theta_i}{2}\right|\left|\varepsilon\right\rangle_i, \tag{1}$$

where i is a sublattice number, $|\theta\rangle_i$, $|\varepsilon\rangle_i$ are the eigenfunctions of orbital ^5E multiplet, Θ_I is an orbital mixing angle, dependent upon local oxygen octahedra distortions, non-local and non-linear effects [12, 13].

The orbital order of Mn^{3+} sublattice within the ac-plane is formed due to intermediate Mn4+ ions shifts along c-direction [15]. The neighbouring ac-planes represent the same charge and orbital arrangement. The charge/orbital structure, supposed in this paper, is drawn on figure 1. The alternation of orbital wave function for different sublattices is as follows [13,14]:

$$\begin{aligned}
\Psi_1 &= \left|\cos\frac{\Theta_1}{2}\right|\left|\theta\right\rangle_1 + \left|\sin\frac{\Theta_1}{2}\right|\left|\varepsilon\right\rangle_1, \\
\Psi_2 &= \left|\cos\frac{\Theta_2}{2}\right|\left|\theta\right\rangle_2 - \left|\sin\frac{\Theta_2}{2}\right|\left|\varepsilon\right\rangle_2, \\
\Theta_1 &= \Theta, \Theta_2 \approx 2\pi - \Theta_1 = 2\pi - \Theta.
\end{aligned} \tag{2}$$

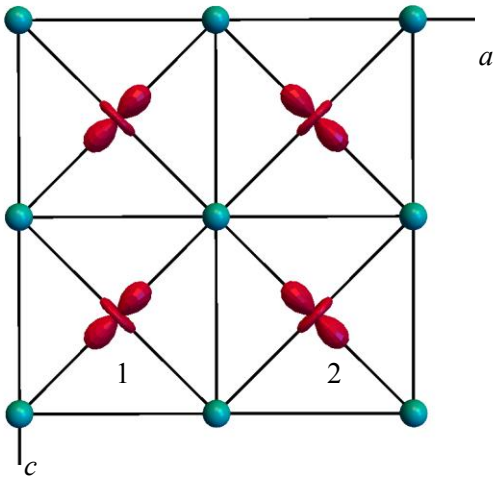


Figure 1. Charge and orbital orderings of half-doped manganite in *ac*–plane. The spheres denote Mn^{4+} ions, the Mn^{3+} ions are drawn as electronic orbitals, numbers denote crystal and orbital sublattices of Mn^{3+}. The adjacent plane is of the same ordering.

2.2. Superexchange interaction and magnetic structure

The Hamiltonian of magnetic subsystem is as follows:

$$\hat{H}_{mag} = \sum_{i>j} J_{ij}(\Theta_i, \Theta_j)\left(\mathbf{S}_i \cdot \mathbf{S}_j\right) + \sum_{i,\alpha,\beta} D_i^{\alpha,\beta}(\Theta_i) S_i^{\alpha} S_i^{\beta}, \quad (3)$$

where first sum is superexchange interaction, second one is single ion. All terms are dependent upon total manganese spins $\mathbf{S}_i$, $\mathbf{S}_j$ and orbital structure parameters Θ_i, Θ_j; i, j are magnetic ions numbers, α, β=x, y, z are Cartesian coordinates. The details of other parts of equation (3) are given below. There are four kinds of superexchange (SE) pairs in CO compounds:

1. Mn^{3+}–Mn^{3+} SE along b-axis

$$J_{ij}^{b}(\Theta_i, \Theta_j) = \frac{J_0^{(1)} \cos^2 \varphi_{ij}}{r_{ij}^{10}} (1 - \alpha(\cos\Theta_i + \cos\Theta_j) + \beta \cos\Theta_i \cos\Theta_j);$$

2. Mn^{3+}–Mn^{4+} in-plane SE

$$J_{ij}^{ac} = \frac{J_0^{(2)} \cos^2 \varphi_{ij}}{r_{ij}^{10}} \left(1 + \alpha'/2 \left(\cos\Theta_i \pm \sqrt{3}\sin\Theta_i\right)\right); \quad (4)$$

3. Mn^{4+}–Mn^{4+} orbitally-independent SE

$$J_{ij}^{b,ac} = \frac{J_0^{(3)} \cos^2 \varphi_{ij}}{r_{ij}^{10}};$$

4. weak SE interaction between planes in the case of layered perovskite crystals.

All parameters are dependent upon SE bond configuration (φ_{ij} is Mn–O–Mn bond angle, r_{ij} is average Mn–O distance of the interacting ions pair, i, j are magnetic ions numbers). The dependence of constants $J_0^{(k)}$, α, α', β could be found using experimental data [14, 15].
Parameters of the dependence are approximately equal to [7, 14]

$$J_0^{(1)} = 1.2 \cdot 10^3 \text{ meV} \times \text{Å}^{10}, \ \alpha = 1, \ \beta = 4.5;$$
$$J_0^{(2)} = -2.6 \cdot 10^3 \text{ meV} \times \text{Å}^{10}, \ \alpha' = 2.8; \quad (5)$$
$$J_0^{(3)} = 1.0 \cdot 10^3 \text{ meV} \times \text{Å}^{10}.$$

The values of in-plane FM interactions within zigzag chains differ 4.5 times from between zigzag chains ones. Thus, the quasi-1D magnetic structure is supposed [14].

In current work, the parameters of in-plane Mn^{3+}–Mn^{4+} superexchange interaction are fitted using experiments [9–11] more carefully.

Taking into account charge and orbital orderings of half-doped compound, which are mentioneed in equation (2) and drawn on figure 1, the parameters of equation (4) could be notated as $J_1^{b}(\Theta) = J_{ij}^{b}(\Theta, 2\pi - \Theta)$, $J_{1,2}^{ac}(\Theta) = J_{ij}^{ac}(\Theta, 2\pi - \Theta)$, $J_2^{b} = J_{ij}^{b}$. Orbital dependences of these parameters are drawn on figure 2.

The dependence of figure 2 is mostly symmetric about Θ=π line. It represents three possible magnetic structures in the crystal. Those are G-type structure (160°<Θ<200°), CE-type structure (40°<Θ<160° and 200°<Θ<320°, the both ranges may be of the one orbital structure with two Mn^{3+} sublattices), and A-type structure (Θ<40° and Θ>320°, the both ranges may be of the one orbital structure with two Mn^{3+} sublattices). Because the interlayer weak exchange interaction is of AFM character [4–6] and SE interaction between ac- planes could not change its sign, there is no difference in magnetic structure types for 3D and layered manganites.

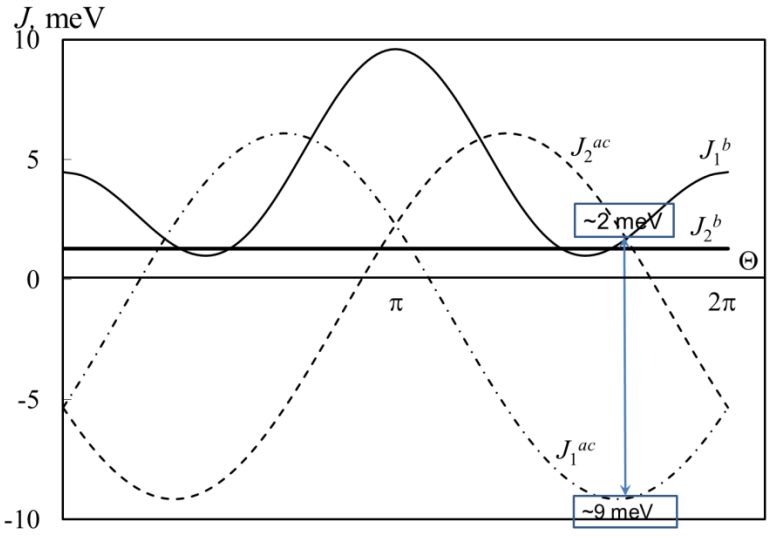


Figure 2. SE parameters dependence upon orbital ordering angle Θ. The frames indicate values of SE parameters in half-doped CO manganite compounds [14].

The single-ion anisotropy (SIA) and the Zeeman interaction are is also orbitally dependent for Mn^{3+} sublattices [15] :

$$H_{an}^{(i)} = D_i S_{iz_\ell}^2 + E_n \left(S_{ix_\ell}^2 - S_{iy_\ell}^2 \right), \qquad (6)$$
$$D_i = -3P\cos\Theta_i\,,\ E_i = -\sqrt{3}P\sin\Theta_i\,,$$

where P=–0.1 meV, ℓ denote the local axes of ith oxygen octahedron.

This interaction forms the diagonal matrix $D_i^{\alpha\alpha}$ of Hamiltonian (3) in the case of coinciding of local and general axes. Because of difference between crystal structure's main direction a, b, c and pseudoperovskite axes as well as presence of oxygen octahedra tilting distortion, the non-diagonal elements of matrix $D_i^{\alpha,\beta}$ appear.

The Mn^{4+} sublattices are supposed without single-ion anisotropy.

3. Results and discussion

In the Table 1, the crystalline structure and SE interaction parameters of compounds under consideration are collected.

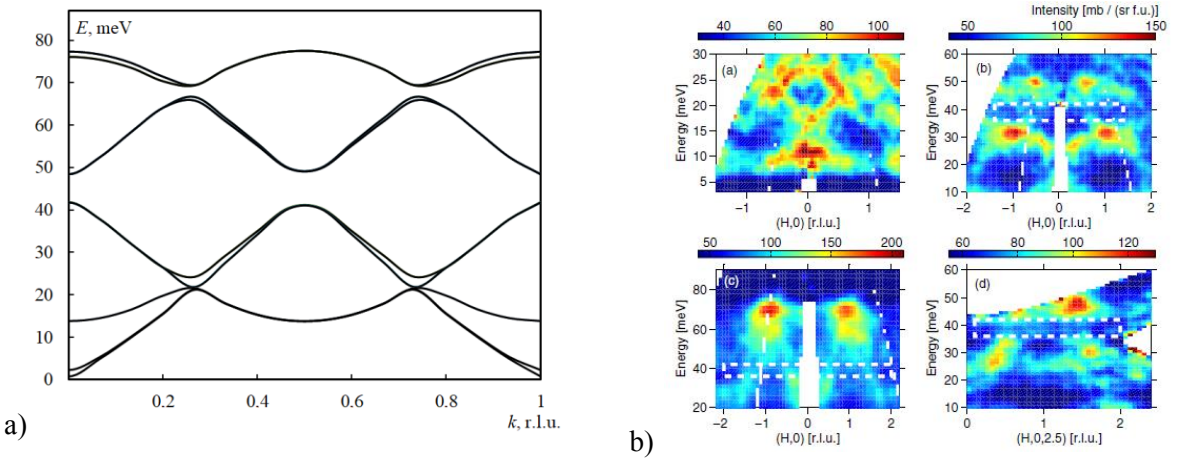
Table 1. SE interaction parameters in different half-doped charge-ordered manganites compounds. The orbital function parameter Θ and SE bond parameters (φ_{ij}, r_{ij}) are used from experimental papers in "[]" beneath compound formula.

Compound	**Θ, deg**	**SE bond config. (φ_{ij}, r_{ij})**	***J***
$La_{0.5}Ca_{0.5}MnO_3$[3]	300, 60	158^0, 2.0 Å	J_1^{ac}=–100 K, J_2^{ac}=12 K, J_1^b=27 K, J_2^b=15 K
$LaSr_{0.5}Sr_{1.5}MnO_4$[4, 5]	300, 60	180^0 2.0 Å	J_1^{ac}=–120 K, J_2^{ac}=15 K, J_1^b=0 K, J_2^b=15 K
$LaSr_2Mn_2O_7$ [6]	300, 60	2.0 Å	J_1^{ac}=–120 K, J_2^{ac}=15 K, J_1^b=27 K, J_2^b=15 K

The equilibrium magnetic structure in SE configuration of Table 1 is CE-type structure, which consists of strongly coupled ferromagnetic (FM) zigzags along *a*-axis, ordered antiferromagnetically (AFM). In the Table 1, $J_{1,2}^{ac}$ are SE parameters in the pairs Mn^{3+}–Mn^{4+} within *ac*-plane, J_1^b is SE parameter in the pairs Mn^{3+}–Mn^{3+} along *b*-axis, J_2^b is SE parameter in the pairs Mn^{4+}–Mn^{4+} along *b*-axis.

Within the framework of linear spin wave approximation and using Hamiltonian (3), the dispersion dependencies of spin-wave spectra are calculated.

The spin-waves spectra along zigzag direction ([1 0 0] direction of reciprocal space) have peculiar features. Some calculated dispersion dependencies of spin-waves are drawn on figures 3-5.



a) b)

Figure 3. a) Calculated spin-wave dispersion of $La_{0.5}Ca_{0.5}MnO_3$ in [*k* 0 0] direction. b) Experimental data of the same dispersion in $Pr_{0.5}Ca_{0.5}MnO_3$ [11], for comparison.

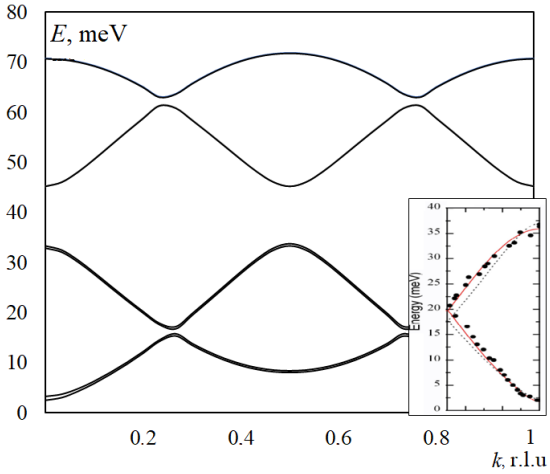


Figure 4. Calculated spin-wave dispersion of $La_{0.5}Sr_{1.5}MnO_4$. in [*k* 0 0] direction. Inset: Experimental data of the same dispersion [9], for comparison.

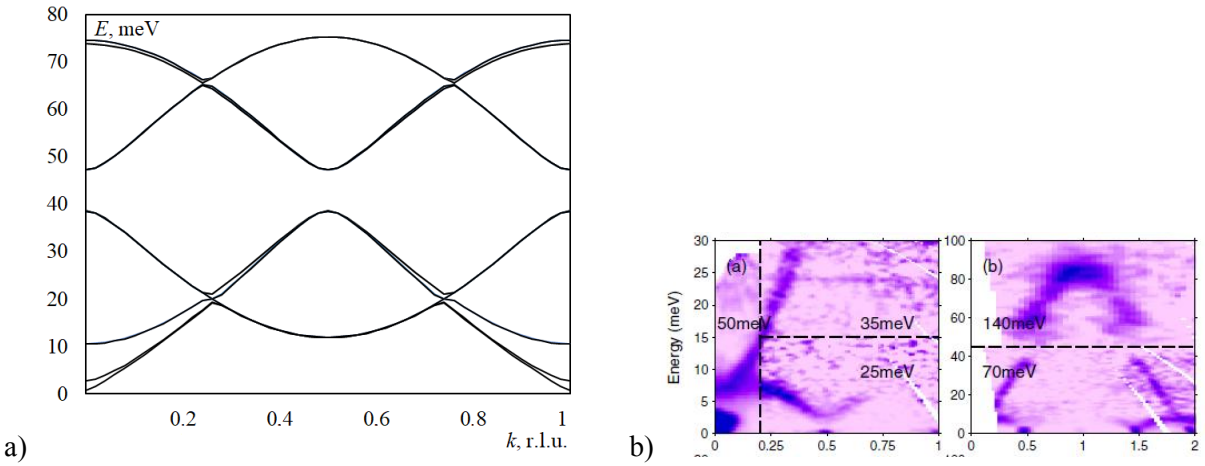


Figure 5. a) Calculated spin-wave dispersion of $LaSr_2Mn_2O_7$ in [k 0 0] direction. b) Experimental data of the same dispersion [10], for comparison.

The influence of strong FM interaction within the zigzag stripe one could see only in dispersion energy scaling [8,14]. Zigzag-like stripes lead to doubling of magnetic cell along a-axis.

The main feature of the SW dispersion of half-doped CO manganites is a wide gap in 30-50 meV zone. It's width depends upon in-plane SE interaction and SIA. The account of octahedra tilting in SIA makes the gap narrower.

If $J^b \neq 0$ could be considered (cases figure 3, figure 5 – 3D and bilayer CO manganites), the lowest branches of spectrum split about 10 meV. One could compare the dispersions near k=0 on figure 3, 5 ($J^b \neq 0$) with figure 4 ($J^b \approx 0$). The spitting leads to appearance of low-energies branches near Γ-point of magnetic Brillouin zone, which are not dependent upon J^{ac} SE interaction. Thus, the AFMR spectra depend only upon J^b and SIA parameters. The low-energies AFMR spectra could not be predicted in the case of $La_{0.5}S_{1.5}MnO_4$. Dispersion dependences are in a good qualitative agreement with experimental data [9–11]. The low-energy branches in AFMR are detected in experimental paper [16], but the authors of [10] neglect this range of spectrum in spite of their experimental data.

The changes of orbital structure parameters in vicinity of $\Theta \approx 300°$ do not lead to any qualitatively changes of the spin-wave dispersion. The drastic change of magnetic structure could be reached at $\Theta \geq 320°$ (see figure 2), where one of planar SE parameters changes its sign.

In spite of quasi-1D character of SE interaction, there is no qualitative difference in features of dispersion dependences in the considered reciprocal space direction comparing with other relation between in-plane and interplanar SE parameters [8, 14].

The authors of experimental papers [9–11] use J_4 FM SE interaction between Mn^{4+} along zigzag chain to make dispersion model closer to experiment. There are no microscopic reasons to take into account so long-range interaction. Nevertheless, it is a trend in modelling of CO and DE manganites [9–11, 17,18]. If one would consider any interaction besides nearest-neighbor SE coupling in half-doped CO manganites, the orbital dependence of that interaction should be proposed. This investigation is out of interest for current study.

4. Summary

The spin-wave dispersion dependencies of half-doped charge ordered manganites are calculated. The analysis of SE interaction between a set of manganese pair upon the form of dependence is held. In 3D and bilayer half-doped manganite, the low-energy spin-wave branches are predicted. The energies of these branches are dependent mainly upon interplanar SE interaction and SIA. They could be experimentally studied by AFMR method in order to estimate magnetic anisotropic interactions. The

in-plane SE interaction gives rise to high-energy dispersion with wide gap between two spin-waves zones.

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